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Electrochemical Systems

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Introduction

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Since the fundamental aspects of electrochemistry are to be developed, in order, in Parts A, B, and C, this chapter has been designed to introduce important concepts related to the flow of fluids, mass transfer, interfacial phenomena, and electrochemical thermodynamics. For accomplishing this purpose, it seems appropriate to begin with a superficial consideration of the behavior of a particular electrochemical system. In this way the reader can see how these factors act, and interact with each other, to determine system behavior. He can then proceed with an overall view of the ultimate utility and application of the detailed material as it is presented subsequently. Since essentially all the material in Chapter 1 will be repeated later with a more thorough development, reference to original work and collateral reading will be postponed.

1.1 THERMODYNAMICS, ELECTRODE KINETICS, AND TRANSPORT PROCESSES

The analysis of electrochemical systems draws primarily on three fundamental areas of electrochemistry.

Thermodynamics provides the framework for describing the properties of electrolytic solutions and their dependence on composition, temperature, and pressure. This is a macroscopic science and hence provides an appropriate basis for our studies, since the system behavior need not be correlated with microscopic or molecular concepts. Thermodynamics also provides a

framework for describing reaction equilibria and thermal effects, which manifest themselves most directly in equilibrium cell potentials. Furthermore, the driving forces for irreversible processes are conveniently expressed in thermodynamic terms.

Departures from equilibrium conditions are inherent in the application of electrochemical systems. *Electrode kinetics* concerns the nonequilibrium driving force, or *surface overpotential*, necessary to make heterogeneous electrode reactions proceed at appreciable rates. Here again, we seek to express relationships among macroscopically measurable quantities as they will affect system behavior.

Of equal importance are irreversibilities associated with *transport* in electrolytic solutions. These are responsible for ohmic losses and heating in the solutions, and for limited rates of transfer of reactants to electrodes and products away from electrodes.

1.2 ROTATING CYLINDERS

To illustrate the applications of these fundamental areas of thermodynamics, electrode kinetics, and transport phenomena, Chapter I will consider their use in the analysis of a simple electrochemical system; namely, two concentric, cylindrical electrodes with an electrolytic solution in the annulus between the two, as shown in Figure 1.1. The application of an

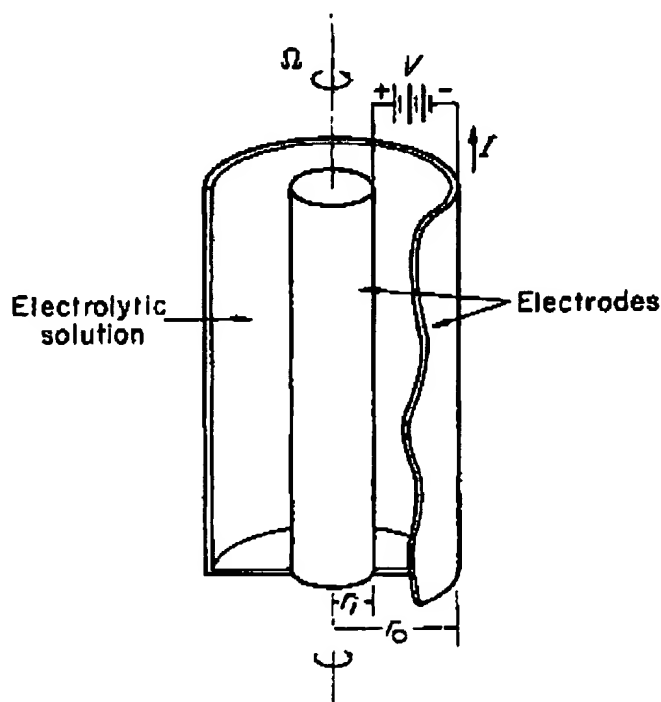


Figure 1.1 System of cylindrical electrodes, the inner of which can rotate.

responds to subtracting the ohmic contribution that would exist in the absence of concentration variations. This definition of concentration overpotential differs from the preceding one by the integral in equation 1.24, which is the difference in the ohmic contribution with and without concentration variations. This term can thus be logically associated with concentration variations near electrodes.

In the present case, with the conductivity related to the concentration by equation 1.6 and with an assumed linear variation of concentration in the diffusion layer, the concentration overpotential can be expressed as

$$\eta_c = \frac{RT}{F} \left[\ln \frac{c_0}{c_b} + t_+ \left(1 - \frac{c_0}{c_b} \right) \right], \quad (1.25)$$

where c_0 refers to the concentration immediately adjacent to the surface of the working electrode.

One of the advantages of this modified definition of the concentration overpotential stems from the fact that the potential difference $\Phi_1 - \Phi_2$ can now be expressed as

$$\Phi_1 - \Phi_2 = \Delta\Phi_{ohm} + \eta_c(\text{anode}) - \eta_c(\text{cathode}), \quad (1.26)$$

where in this case $\Delta\Phi_{ohm}$ can be calculated without regard for the concentration variations near electrodes and is, in fact, given by equation 1.10. The difference between these two definitions is probably not important except for solutions of a single electrolyte, such as the cupric sulfate solutions being considered here. In detailed calculations for many electrochemical systems, it is desirable to calculate the potential distribution in the bulk solution somewhat separated from the details of the calculations of concentration variations near electrodes. The principal disadvantage of the second decomposition of potentials lies in the fact that it is different from the decomposition of potential differences by interrupter methods.

Figure 1.9 shows the concentration overpotential at a cathode for currents up to the limiting current.

1.8 SURFACE OVERPOTENTIAL

An additional contribution to the overall cell potential is the driving force required to make the electrode reactions proceed at appreciable rates. The *surface overpotential* is defined as the potential of the working electrode relative to a reference electrode of the same kind placed in the solution adjacent to the surface of the working electrode. This reference electrode is thus one of those used to define the concentration overpotential. For example, at the anode in Figure 1.8, the surface overpotential is

$$\eta_s = \Phi(\text{anode}) - \Phi_1. \quad (1.27)$$

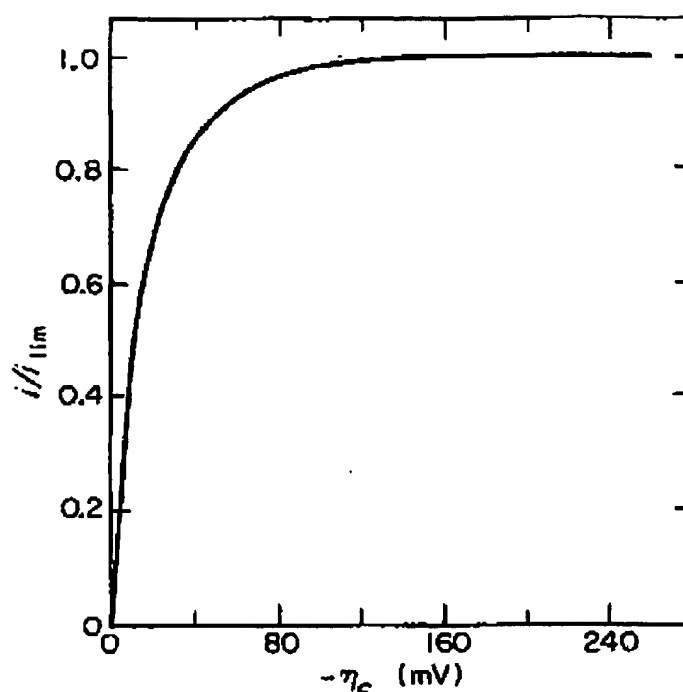


Figure 1.9 Concentration overpotentials at a cathode in 0.1 M CuSO_4 .

The rate of the electrode reactions is the rate of dissolution or deposition of copper, and this can be conveniently measured by the current density at the electrode. By convention, the current density is positive when it flows from the electrode into the solution. Thus, current densities are positive at anodes and negative at cathodes.

The current density depends on the driving force and thus is related to the surface overpotential and the composition of the solution at the interface, as well as the temperature. For example, the current density can frequently be expressed as

$$i = i_0 \left[\exp \left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp \left(- \frac{\alpha_c F}{RT} \eta_s \right) \right]. \quad (1.28)$$

This is similar to the expression of the rate of a nonelectrochemical, heterogeneous reaction. The first exponential term can be regarded as representing the rate of the anodic process, and the second term, that of the cathodic process. These are governed by activation energies which depend on the surface overpotential.

When $\eta_s = 0$, the anodic and cathodic currents are equal in magnitude to each other and to i_0 . This is an important kinetic parameter and is termed the *exchange current density*. Different reactions may have exchange current densities that differ by many orders of magnitude. Furthermore, the exchange current density depends strongly on the composition at the interface

and on the temperature. α_a and α_c are two additional kinetic parameters and may be termed *apparent transfer coefficients*. They usually have values between 0.2 and 2.

Equation 1.28 serves to show explicitly a typical dependence of reaction rate on surface overpotential. The dependence on composition and temperature is not shown explicitly, since i_0 depends on these factors in an unspecified manner. Many reactions, such as those involving oxide formation, are complicated and do not follow equation 1.28. Even the relatively simple copper electrode is complicated. At high anodic rates, appreciable amounts of cuprous ions are formed. These subsequently disproportionate in the solution to yield cupric ions and copper, which precipitates,



It should also be noted that the value of i_0 can depend on the composition and preparation of the electrode and on the presence of impurities.

With these words of caution, we introduce equation 1.28 to describe electrochemical kinetics in general or in the absence of detailed information. It should be emphasized that the goal here is to relate the reaction rate or current density to conditions prevailing at the interface itself. Thus, we define the surface overpotential in terms of a reference electrode well within the diffusion layer, adjacent to the electrode surface; and we seek to relate the kinetic parameters to the composition adjacent to the electrode, not to the composition of the bulk solution or to concentration gradients near the surface.

The exchange current density is a measure of the freedom from kinetic limitations. A reaction with a large value of i_0 is frequently said to be *fast* or *reversible*. For large values of i_0 , a given current density can be obtained with small surface overpotentials.

Figures 1.10 and 1.11 illustrate the behavior of equation 1.28. One can see that higher values of i_0 give higher values of the current density at a given surface overpotential. Figure 1.11 is a so-called Tafel plot, used because, at high surface overpotentials, one of the terms in equation 1.28 becomes negligible, and a straight line is obtained on a semilogarithmic plot. Thus

$$i = i_0 \exp \left(\frac{\alpha_a F}{RT} \eta_s \right) \quad \text{or} \quad \eta_s = 2.303 \frac{RT}{\alpha_a F} \log \frac{i}{i_0} \quad (1.30)$$

for $\alpha_a F \eta_s \gg RT$;

$$i = -i_0 \exp \left(-\frac{\alpha_c F}{RT} \eta_s \right) \quad \text{or} \quad \eta_s = -2.303 \frac{RT}{\alpha_c F} \log \left| \frac{i}{i_0} \right| \quad (1.31)$$

for $\alpha_c F \eta_s \ll -RT$.

The *Tafel slope*, either $2.303 RT/\alpha_a F$ or $2.303 RT/\alpha_c F$, is thus seen to be inversely proportional to the apparent transfer coefficients.